

Determination of 21 Trace Impurities in High-Purity Ammonium Paratungstate by the Agilent High-Matrix Introduction Accessory for the 7500cx ICP-MS

Application Note

Semiconductor

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Abstract

A simple, robust, and reliable method has been developed for the measurement of 21 trace elements in high-purity ammonium paratungstate (APT) using an Agilent 7500cx ICP-MS fitted with a High Matrix Introduction (HMI) system. HMI is a new sample-introduction accessory specially designed for concentrated samples with high total dissolved solids (TDS). Comparing results obtained using different APT sample digestion methods shows that dissolving the material in heated 4% H_2O_2 minimizes the formation of interferences on difficult elements such as phosphorus and silicon. APT samples containing 1% TDS were analyzed directly using the HMI's ultra robust mode. Results were calculated using the method of standard addition (MSA). Interferences on challenging elements such as Ca, K, Fe, and Si were removed by the Octopole Reaction System (ORS), a standard component of the Agilent 7500cx. The short turnaround time, including sample preparation and analysis time, indicates that the method is suitable for onsite testing.



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Introduction

Ammonium paratungstate (APT) is an important intermediate in the production of tungsten trioxide (WO_3) and tungsten metal, both of which are used in the semiconductor and electronic industries. As the properties of these materials are strongly affected by elemental impurities, [1] it is necessary to assess the purity level of any intermediaries used in their manufacture as well as the materials themselves. Elements of interest include Na, K, Ca, Fe, Si, P, and S.

Traditional analytical techniques for the analysis of high-purity tungsten are graphite furnace atomic absorption spectroscopy (GFAAS), flame atomic absorption spectroscopy (FAAS), and inductively coupled plasma optical emission spectroscopy (ICP-OES) [1–6]. However, direct determination of high-purity tungsten by these methods has been limited by the formation of intense matrix interferences. Analyte/matrix separation methods, such as ion exchange, liquid-liquid extraction, and co-precipitation have been investigated for the analysis [1–6] but these matrix elimination methods are time-consuming, labor-intensive, and costly. They also increase the risk of contamination and the loss of key trace elements. Consequently, a more powerful and reliable method is required for the determination of trace contaminants in high-purity tungsten.

ICP-MS is frequently used for high-purity materials testing because of its superior sensitivity and low detection limits compared to the traditional analytical techniques. However, this application remains challenging for conventional ICP-MS for the following reasons:

- Deposits from high-matrix ($\text{TDS} > 0.1\%$) samples build up on the interface cones, resulting in signal drift and instability.
- Possible contamination from ubiquitous elements such as Na, K, Al, Ca, and Fe during sample preparation or dilution. Dilution also degrades detection limits.
- Serious interferences on K, Ca, Fe, Si, P, and S
 - Polyatomic ion interferences from ArH^+ , Ar^+ , ArO^+ , N_2^+ , O_2^+ , and NOH^+
 - Memory effects for elements such as Li and Na from the interface cones

The Agilent High Matrix Introduction (HMI) system has been developed specifically for the analysis of high-matrix samples. For the first time, samples with high TDS (up to 1%) can be

introduced into an Agilent HMI/ICP-MS without causing signal drift problems [7]. HMI increases the effectiveness of sample dissociation in the ICP central channel and improves ionization efficiency by means of aerosol gas dilution. Aerosol dilution reduces the amount of sample that is transported into the ICP, which means that the amount of solvent vapor (usually water) reaching the plasma is also reduced. With less water to decompose, the plasma is hotter and therefore more robust [illustrated by the reduced CeO^+/Ce^+ ratio ($< 0.2\%$)]. Furthermore, the Octopole Reaction System (ORS) of the Agilent 7500 Series ICP-MS uses simple, universal conditions to remove polyatomic interferences effectively. The combination of these two advanced technologies is key to improving the ability of ICP-MS to run very high and variable matrix samples routinely and accurately.

In this study, a new method has been developed for the determination of 21 metal impurities in high-purity APT using the Agilent 7500cx ICP-MS fitted with an HMI. The methodology is suitable for quality control, certification, and evaluation of APT on the production line.

Experimental

Reagents

- Hydrogen peroxide H_2O_2 (microelectronic grade); ammonium hydroxide NH_4OH (microelectronic grade); ultrapure water (18.2 MW)
- Standard stock solution: 10 $\mu\text{g}/\text{mL}$ mixed standard solution including Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, As, Cd, and Pb (Agilent p/n 8500-6940)
- 7500 Series PA Tuning Solution 2 including 10 $\mu\text{g}/\text{mL}$ Mo, Sn, Sb, and 5.0 $\mu\text{g}/\text{mL}$ Ti (Agilent p/n 5188-6524)
- 1,000 $\mu\text{g}/\text{mL}$ S standard solution (High-Purity Standards, Charleston, SC, USA)
- 1,000 $\mu\text{g}/\text{mL}$ P standard solution (High-Purity Standards, Charleston, SC, USA)
- 1,000 $\mu\text{g}/\text{mL}$ Si standard solution (High-Purity Standards, Charleston, SC, USA)
- 100 $\mu\text{g}/\text{mL}$ mixed internal standard solution including ^6Li , Sc, Ge, Rh, In, Tb, Lu, and Bi (Agilent p/n 5188-6525).

Instrumentation

An Agilent 7500cx ORS ICP-MS fitted with a new HMI accessory was used throughout the study. Operating parameters are shown in Table 1. The ORS was operated in no-gas and hydrogen modes, with automatic switching, depending on the target analyte. H₂ reaction mode was selected to remove the intense plasma-based interferences such as ¹⁴N₂⁺ and ¹²C¹⁶O⁺ on ²⁸Si⁺; ³⁸Ar¹H⁺ on ³⁹K⁺; ⁴⁰Ar⁺ on ⁴⁰Ca⁺; and ⁴⁰Ar¹⁶O⁺ on ⁵⁶Fe⁺. All other analytes were analyzed in no-gas mode.

Sample Preparation

APT samples supplied by Xiamen Tungsten Co., Ltd., China, were used as quality control samples. The reference values of the metal content of the samples are a summary of the results obtained using traditional methods, including UV-Vis, AAS, Arc-AES, and GD-MS.

To prepare APT for analysis by ICP-MS, 0.500 g of APT was weighed into a polypropylene vessel. The samples were heated in approximately 40 mL 4% NH₄OH (or 4% H₂O₂) solution and then kept in a water bath at 80 °C until all the solid material had dissolved (about 15 minutes). Once cool, 50 µL of 10 µg/kg internal standard (ISTD) solution was added. A 4% NH₄OH (or 4% H₂O₂) solution was then added until the total solution weighed 50.00 g. In this final solution, APT samples are 100 times diluted to a TDS level of about 1% and the internal standard concentration 10.0 µg/kg.

Calibration

Analyses were performed using the method of standard addition (MSA). Calibration stock solutions containing Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, As, Cd, Mo, Sn, Sb, and Pb at 0, 10, 20, 40, and 60 µg/kg were spiked directly into randomly selected 1% APT solutions. The spiked concentrations for Ti were 0, 5, 10, 20, and 30 µg/kg and 0, 20, 40, and 80 µg/kg, respectively, for Si and P. ISTD correction based upon mass-interpolated virtual internal standards (VIS)* was applied. The MSA calibrations were converted into external calibrations using the inbuilt software function. The trace metal content of all other APT samples was then determined using the external calibrations. Concentrations obtained were corrected to account for the dilution factor.

Results and Discussion

Sample Digestion

APT is soluble in NH₄OH and H₂O₂ but insoluble in acid and water. A 4% ammonium hydroxide solution is often the first choice for APT digestion. However, as NH₃ induces N-based polyatomic interferences on ²⁸Si (by NN⁺) and ³¹P (by NOH⁺), 4% H₂O₂ was investigated as an alternative digestion medium.

*VIS is a unique feature of the Agilent ICP-MS ChemStation and new MassHunter software. It allows the user to define a mass-interpolated internal standard (ISTD) at any mass in order to eliminate the errors arising from the mass difference between ISTDs and analytes. The result is more accurate ISTD correction.

Table 1. Operating Conditions of Agilent HMI/7500cx ICP-MS

Parameter	Setting	Parameter	Setting
Sampling and skimmer cones	Nickel	Plasma conditions	Ultra robust
Nebulizer	200-µL/min PFA microflow	Aerosol reduction level	High
RF power	1600 W	Sampling depth	10 mm
Plasma gas	15.0 L/min	Integration time	1 s
Carrier gas	0.38 L/min	Number of replicates	3
HMI dilution gas	0.64 L/min	Sample uptake rate	0.4 mL/min
S/C temperature	2.0 °C	Reaction gas (H ₂)	4.0 mL/min

Table 2. Comparison of Concentrations (calculated back to the solid) of APT Samples Prepared Using 4% NH₃ and 4% H₂O₂ Digestion Methods, Respectively (All units: mg/kg)

Element	Mode	APT05 (NH ₃)	APT05 (H ₂ O ₂)	Reference	APT06 (NH ₃)	APT06 (H ₂ O ₂)	Reference
23 Na	No gas	1.9	—	1.9	2.3	—	2.1
24 Mg	No gas	0.02	0.13	< 1	0.09	0.29	< 1
27 Al	No gas	0.03	0.09	< 5	0.04	0.23	< 2
28 Si	H ₂	0.99	0.26	< 4	0.80	2.0	< 4
31 P	No gas	—	1.7	1.6	—	1.1	1.0
39 K	H ₂	4.5	3.1	4.9	5.1	4.7	5.0
40 Ca	H ₂	0.52	0.23	< 1	0.55	0.56	< 3
47 Ti	H ₂	0.00	0.02	< 1	0.00	0.10	< 2
51 V	No gas	0.001	0.013	< 1	0.02	0.02	< 1
52 Cr	H ₂	0.07	0.03	< 1	0.04	0.05	< 1
55 Mn	H ₂	0.008	0.012	< 1	0.01	0.14	< 1
56 Fe	H ₂	0.001	0.24	< 2	0.015	0.17	< 2
59 Co	H ₂	0.01	0.00	< 1	0.01	0.01	< 1
60 Ni	No gas	0.07	0.03	< 2	0.38	0.04	< 3
63 Cu	No gas	1.1	1.2	1.5	1.2	1.3	1.6
75 As	No gas	2.8	2.8	< 5	1.2	1.5	< 5
95 Mo	H ₂	11	10	11.6	9.0	8.5	9.1
111 Cd	No gas	0.010	0.007	< 1	0.000	0.010	< 1
118 Sn	No gas	2.2	2.0	2.1	1.4	1.3	1.9
121 Sb	No gas	0.10	0.058	0.2	2.6	2.0	2.3
208 Pb	No gas	0.09	0.10	< 1	0.09	0.13	< 1

APT solutions prepared in NH₄OH and H₂O₂ were analyzed directly by HMI/ICP-MS. The major impurities include Na, K, Mo, Cu, Sn, and Sb (Table 2). Both 4% NH₃ and 4% H₂O₂ digestion methods show good agreement with the reference values. While the ORS will remove nitrogen interferences (NOH⁺ interferes with P), a small deterioration of detection limit for P was noted. To reduce the risk, 4% H₂O₂ is preferred for APT digestion.

Interference Removal

The 7500cx features an ORS collision/reaction cell to remove interferences that inhibit the analysis of some elements of interest. The ORS was operated in H₂ reaction mode to eliminate the polyatomic interferences on Si, K, Ca, Cr, and Fe.

Method Detection Limits

Method detection limits (MDLs) were calculated from seven repeated measurements of an APT sample rather than by measuring the reagent blank. MDL results by matrix are more representative of the actual method. The MDLs exceed the industry-required specifications for APT products (see right-hand column of Table 3) and are sufficient for routine analysis of APT products.

Sample Analysis

Results obtained from the analysis of six high-purity APT reference samples using the new HMI/ICP-MS method are shown in Table 3. The results of major impurities such as Na, P, K, As, Mo, Sn, and Sb agree well with the reference values. The ICP-MS MDL results obtained for the trace impurities are

Table 3. Results of HMI/ICP-MS Analysis of Ammonium Paratungstate Compared to Reference Samples. CSAPT0 represents the industrial specifications for APT. [All units: mg/kg]

Elem	APT457	Ref.	APT045	Ref.	APT577	Ref.	98353	Ref	APT05	Ref.	APT06	Ref	MDL	CSAPT0
23 Na	2.9	2.5	3.0	1.8	3.1	2.8	–	–	–	1.9	–	2.1	–	–
24 Mg	0.24	< 1	0.024	< 1	0.12	< 1	0.13	–	0.13	< 1	0.29	< 1	0.01	< 7
27 Al	0.12	< 1	0.057	< 1	0.10	< 1	0.18	–	0.096	< 5	0.23	< 2	0.06	< 5
28 Si	0.90	< 4	0.42	< 3.5	0.53	< 3	0.78	–	0.26	< 4	2.0	< 4	0.4	< 10
31 P	2.6	2.2	3.4	3.6	4.7	5	7.1	6.4	1.7	1.6	1.1	1.0	0.4	< 7
39 K	4.6	< 6.9	3.2	< 5.7	5.1	< 7.2	4.0	–	3.1	4.9	4.7	5.0	0.5	< 10
40 Ca	0.12	< 2	0.046	< 2	0.11	< 2	0.26	–	0.23	< 1.3	0.56	< 3	0.05	< 10
47 Ti	0.04	< 1	0.049	< 1	0.043	< 1	0.04	–	0.021	< 1	0.10	< 2	0.04	< 10
51 V	0.007	< 1	0.039	< 1	0.007	< 1	0.005	–	0.013	< 1	0.02	< 1	0.002	< 10
52 Cr	0.014	< 1	0.013	< 1	0.015	< 1	0.037	–	0.025	< 1	0.05	< 1	0.01	< 10
55 Mn	0.12	< 1	0.021	< 1	0.12	< 1	0.10	–	0.012	< 1	0.14	< 1	0.003	< 10
56 Fe	0.08	< 2	0.13	< 2	0.087	< 2	0.13	< 2	0.24	< 2	0.17	< 2	0.03	< 10
59 Co	0.003	< 1	0.002	< 1	0.03	< 1	0.024	< 1	0.00	< 1	0.01	< 1	0.001	< 10
60 Ni	0.20	< 2	0.013	< 2	0.20	< 2	0.13	< 2	0.028	< 2	0.04	< 3	0.003	< 7
63 Cu	0.14	0.1	0.14	< 0.1	0.14	< 0.2	0.71	–	1.2	1.5	1.3	1.6	0.09	< 3
75 As	3.5	4.3	3.5	3	3.5	4	3.5	–	2.8	< 5	1.5	< 5	0.09	< 10
95 Mo	9.1	7.9	5.8	7.2	9.1	9.4	11	–	10	11.6	8.5	9.1	0.7	< 20
111 Cd	0.006	< 1	0.005	< 1	0.006	< 1	0.008	< 1	0.007	< 1.5	0.01	< 1	0.004	–
118 Sn	< DL	< 0.1	< DL	< 0.1	< DL	< 0.1	0.49	–	2.0	2.1	1.3	1.9	0.07	< 1
121 Sb	< DL	< 0.2	< DL	< 0.2	< DL	< 0.2	0.004	–	0.058	0.2	2.0	2.3	0.1	< 8
208 Pb	0.11	< 0.2	0.10	< 0.2	0.11	< 0.2	0.14	–	0.10	< 1	0.13	< 1	0.007	< 1

much lower than those obtained using traditional techniques illustrating the capabilities of the HMI/7500cx for this application.

Instrument Stability

The short-term stability of the method was tested by continuously running a 1% APT sample spiked with a 40 µg/kg multi-element standard over 2 hours (equivalent to 25 successive sample measurements). Instrument stability over this period was good, with % relative standard deviation (%RSD) values typically better than 5.0%, except ⁵⁶Fe at < 5.7% (possibly due to oxygen impurities in the H₂ reaction gas). A normalized stability plot, without ISTD correction (to highlight the effectiveness of the HMI), is shown in Figure 1. The extremely good stability results for elements present in such a high-matrix sample illustrate that the method is suitable for routine analysis.

Conclusions

A new robust and sensitive method for the routine analysis of elemental impurities present in high-purity APT has been developed using the new High Matrix Introduction (HMI) sample-introduction device for the Agilent 7500cx ICP-MS. Following a simple and quick sample digestion procedure in 4% H₂O₂, APT sample solutions containing 1% TDS were introduced to the ICP via the HMI. With the development of this new method of sample introduction, high-matrix samples can now be analyzed by ICP-MS, with minimal sample buildup on the interface, as indicated by the excellent 2-hour stability test.

The ORS, an integral component of the 7500cx ICP-MS, was used to attenuate argon and matrix-based interferences on target analytes, including K, Ca, Fe, Si, P, and S using hydrogen and no-gas modes within a single method. The resulting low MDLs exceed industry required limits.

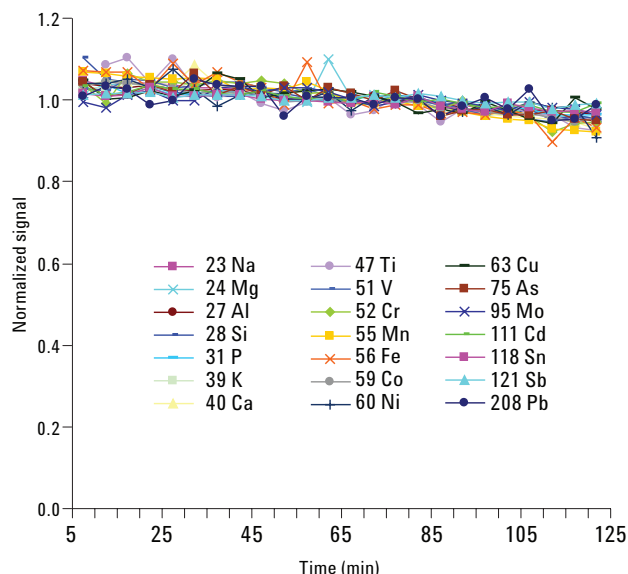


Figure 1. Short-term stability plot based on the analysis of a 1% ammonium paratungstate digest spiked with a 40 µg/kg multielement standard obtained over a 2-hour continuous run (no ISTD correction applied).

This study has shown that the new ICP-MS method has sufficient robustness and sensitivity for the routine analysis of APT samples and is therefore a suitable replacement for the multiple traditional analytical techniques usually used for this application.

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